

# INVESTIGATION OF THE OPERATIONAL PARAMETERS OF THE SUBTERRA METHOD FOR IN SITU IRON-MANGANESE ELIMINATION (WATERWORK HALÁSZTELEK)

by

I. ORSOVAI

Institute of Applied and Engineering Geology, Eötvös Loránd University, Budapest

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## Abstract

Upon the execution and evaluation of programmed tests in a series of driven wells under operation it has been clarified the efficiency of iron-manganese elimination under given hydro-geological conditions.

The characteristic data of the aquifer are:

- Transmissivity:  $(2,5 - 5,0) \cdot 10^{-3}$  m/sec,
- Porosity: 27,85 - 28,37%
- Seepage speed: from the direction of the Danube:  $1,6 - 1,8 \cdot 10^{-5}$  m/sec,  
- : from the direction of the background:  $7,7 - 9,8 \cdot 10^{-5}$  m/sec,
- Distribution of the clay minerals: 50% montmorillonite, 20% kaolinite, 30% illite,
- Ion-exchange capacity: 40 - 60 mekv/100 g,
- The extent of the oxidational zone, on the basis of the measurement of the  $O_2$  in solution: 9,0 - 9,5 m
- Maintainability of oxidational zone: 0,05 mg/l iron after 60 hours, 0,5 mg/l iron after 96 hours.

The extension of the depressed are is different in the two profiles: in Well-8 it is  $R = 3 - 6$  m, and in Well-22 it extends as far as the Danube.

The iron-manganese content of the water arriving from the Danube and from the background differs very little, but water from the Danube has higher concentration.

Due to oversizing (it is approximately twenty fold at the given time-program) it is hard to tell the efficiency numerically, however, according to complementary experiments it is satisfactory.

## Introduction

The Subterra method for in situ iron-manganese elimination of a driven-well was first introduced for operational conditions between May 1985 - October 1986 in the middle part of the Danube valley. Previously, half-operational experiments were carried out in this territory, operating the two neighbouring wells alternatively. The introduction at an operational level started after a series of successful experiments had been done.

To determine the operational parameters the following questions had to be answered:

- The extent of the oxidational zone and the temporal change of the chemical parameters,
- The range of maintaining,
- The extension of the area of water-table lowering by single wells and the well-line,
- Space/time changes in iron-manganese content of the Danube and from the background,
- The efficiency of the process.

### Experimental apparatus and procedure

The operational program (Fig. 1.) was determined by the Subterra method and also the wells had to be installed according to that.

Taking the environments of the wells separately, the plan of the experiments was the following:

The geometrical data had to be determined from the theoretical profile seen in Fig. 3., with the help of the observation wells seen in Fig. 4. It could already be foreseen, and was also confirmed later, that the distance between the observation wells is much too big as compared to the extent of the oxidational zone.

Nevertheless, because of the water mechanical works (collector cable, electric ground cable) the observation wells could not be installed closer to each other than three metres.

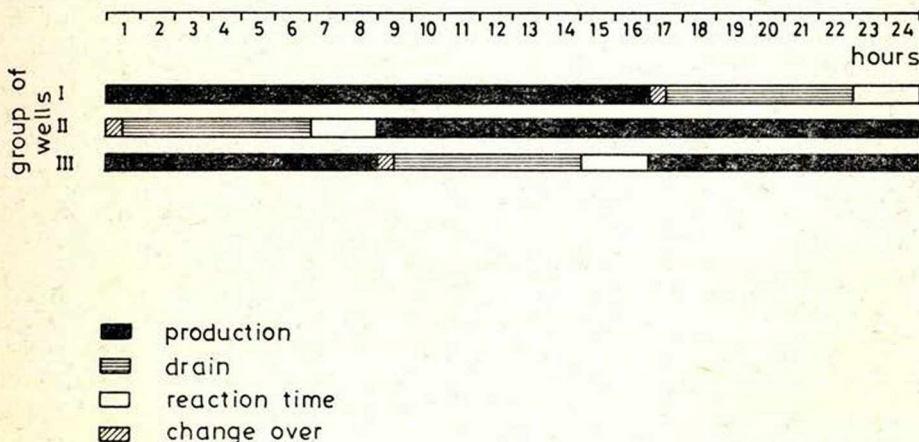


Fig. 1. Daily programme of consolidated process



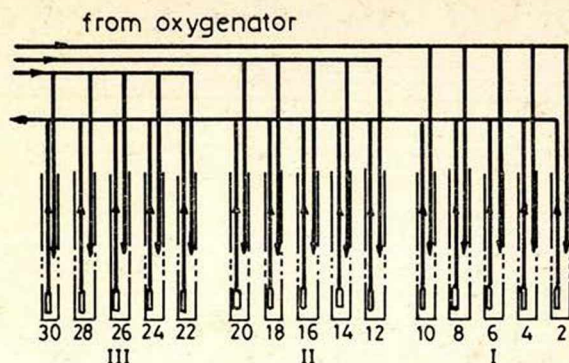
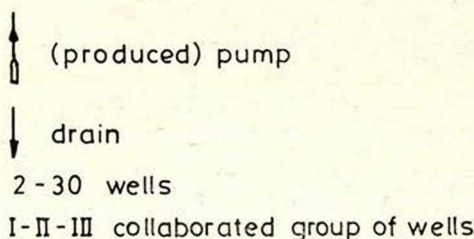


Fig. 2. Functional plan of experiment



### A rough outline of the geological and hydrogeological properties of the aquifer used for iron-manganese elimination process

The impermeable underlying bed is an Upper Pannonian, clayey, sandy, micaceous formation. Its water chemical role is important.

The actual site of the iron-manganese elimination process is a gravelly, sandy, somewhat silty clastic formation, which is stratigraphically the same as the Late Pleistocene – Early Holocene II/a terrace of the Danube. Its fraction above 2 mm of grain-size contains mainly quartzite, various amounts of andesite and an insignificant amount of carbonate rocks (more dolomite with less limestone).

Its transmissivity and pore volume depends on the grain distribution and sorting determining its hydraulical importance too.

Practically it has no direct hydrochemical role, the surface of the grains is inactive. Hydrochemically the grains under 2 mm are most important. These could be examined thoroughly because the whole amount of the material that was brought up from under the water table by drilling, was elutriated, so the loss of the small grain fraction was minimal (Fig. 5.).

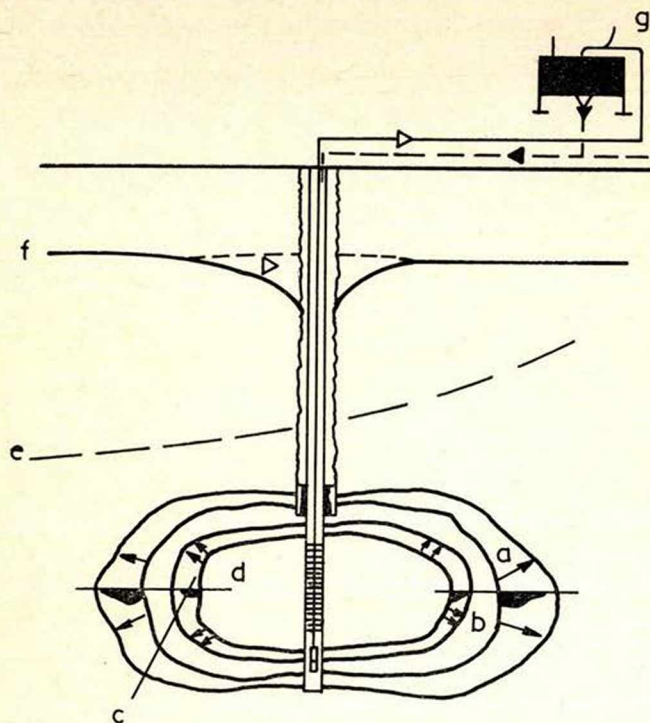


Fig. 3. Plan of oxidation zone

- a. accumulation of iron
- b. zone free from iron
- c. accumulation of manganese
- d. zone free from iron and manganese
- e. limit of  $O_2$  content
- f. water-table
- g. oxygenator

Chemically the silt fraction is most typical of the aquifer. It was separated by means of a sieve of  $20\ \mu\text{m}$  meshes (Fritsch afnor NFX 11-501. No. 14.) by rinsing, according to engineering geological practice. The fraction between  $20-50\ \mu\text{m}$  was also taken under examination if it proved to be active in a way.

The silt content of the sandy gravel can be syngenetic (grains of different distributions settle from the turbulating current) and epigenetic



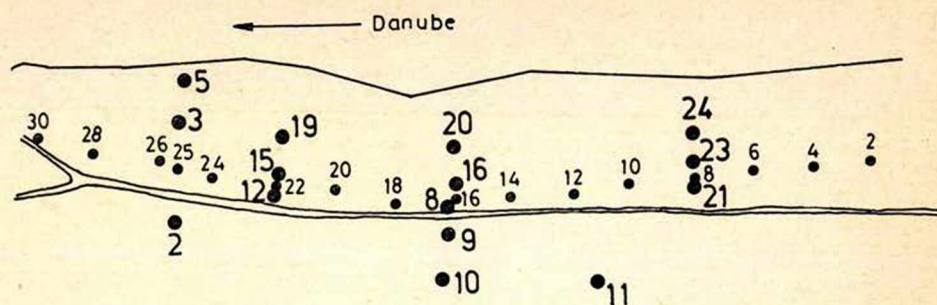


Fig. 4. Locality of experiments

1:5000

- 2-30 producing and drain wells
- 15-19 test wells

through fossil and recent kolmatation. In our case syngenetic sedimentation is typical of the aquifer while recent kolmatation characterizes the river channel, so two different silt types had to be taken into account, differing both genetically and in composition.

The floating fraction of the core samples and the floating matter content of the Danube water are very similar in composition. The difference is the result of diagenesis. The material of the kolmatated channel bottom is substantially different.

	1.	2.	3.
SiO <sub>2</sub>	8,8%	25,2%	15,7%
Al <sub>2</sub> O <sub>3</sub>	4,9	5,2	3,1
Fe <sub>2</sub> O <sub>3</sub>	0,4	14,6	4,3
MnO <sub>2</sub>	—	3,4	1,1
CaO	14,3	12,1	3,7
MgO	2,9	2,6	3,5
Na <sub>2</sub> O	9,8	4,7	7,6
K <sub>2</sub> O	2,1	3,1	2,7
Cl <sup>-</sup>	6,4	6,2	3,1
SO <sub>4</sub> <sup>-</sup>	12,3	13,5	1,8
CO <sub>2</sub>	13,0	11,0	19,6
C <sub>org</sub>	25,0	8,2	37,0
	99,9%	99,8%	100,2%

1. The floating matter of the Danube
2. The fraction above 20  $\mu$ m in diameter of the aquifer
3. Recent Danube channel kolmatating material

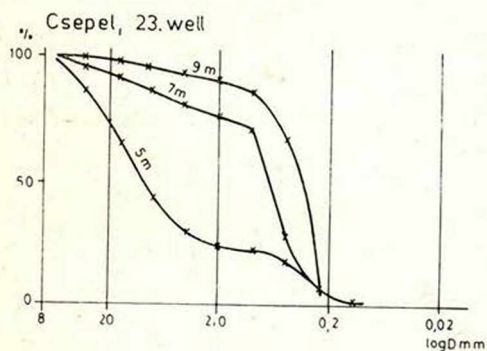
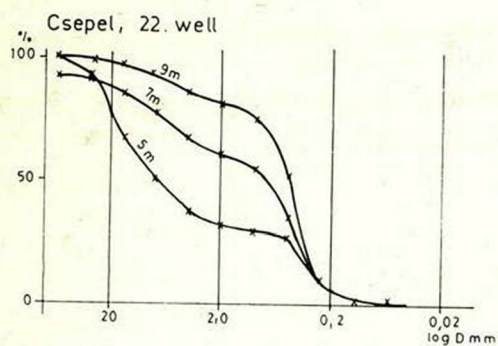
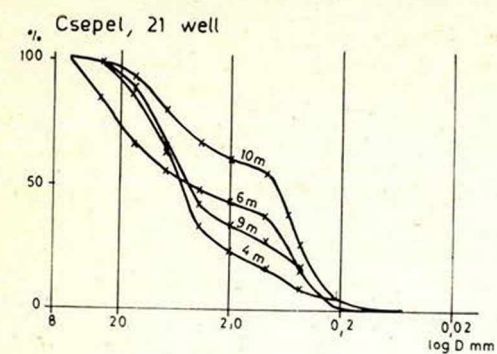


Fig. 5 Characteristic granulometry  
in tested aquifer



The ion-exchange capacity of the clay minerals is moderate; 40–60 mekv/100 g and difficult to measure because it can hardly be separated from the other components of the fraction; even the effective agents of the  $C_{org}$  have surface activity (adsorbition).

According to X-ray analysis the composition of the clay minerals is varied, 50% montmorillonite, 20% kaolinite and 30% illite is typical of them on an average.

On the basis of the examinations it could be firmly concluded that the silt fraction is decisive regarding the iron-manganese transport (stabilization and mobilization or, in a proper sense, restabilization and remobilization). This is not merely the result of the small specific surface which is attributable to the small grain-size and which advances surface-dependent processes (chemisorbition), because the surface activity has much more importance than the specific surface (e. g. ion-exchange, adsorbition catalysis, etc.).

Due to similar causes (small amount and difficulties in separation) the organophilia of montmorillonite could not be measured, therefore our working hypothesis was the following:

The clay mineral and the detritus form separate adsorbition systems, otherwise the two systems would adsorb each other thus disabling the adsorbition capacity.

Indirect measurements made this working hypothesis plausible.

The surface activity of the floating matter has double chemical effects:

a) It promotes some (mainly reductional) chemical processes (chemisorbition, adsorbition catalysis) and accumulates the transformed matters on the surface of the grains,

b) It produces favourable conditions for bacterial functions.

This latter effect is based on the fact that the environmental conditions, needed for the optimum life function of these bacteria, does not meet the actual environmental conditions, and the bacteria can only make permanent micro-conditions (pH, Eh) in the silty rocks, where due to the bad permeability, the small speed of seepage and diffusion does not let the two different chemical environments to mix.

We determined the free pore volume by means of the core samples (28,37% on an average) and also by means of a pumping test, according to the Bindemann – method (27,85%) therefore we calculated with a rounded porosity value of approximately 30% in preliminary planning. This time we measured the seepage also in the directions of the Danube and of the background. Comparing these data with the data obtained in 1981 we got the following results:

place	direction	1981	1981
		speed, $V_{eff}$ (m/sec)	speed, $v_{eff}$ (m/sec)
observation	from the Danube	$1,4 \cdot 10^{-4}$	$1,6 \cdot 10^{-4}$
wells 13–12.	from the background	$1,8 \cdot 10^{-4}$	$9,8 \cdot 10^{-5}$
wells 15–14.	from the Danube	$1,8 \cdot 10^{-4}$	$1,9 \cdot 10^{-4}$
wells	from the background	$7,0 \cdot 10^{-5}$	$7,7 \cdot 10^{-5}$
wells 21–24.	from the Danube	—	$1,8 \cdot 10^{-4}$
	from the background	—	$8,0 \cdot 10^{-5}$

When the measurements were carried out the water level of the Danube was approximately 200 cm in both cases.

Former data for transmissivity in 1981:

producing well–20.:  $K = (4,13–4,18) \cdot 10^{-3}$  m/sec

producing well–22.:  $K = (2,50–2,64) \cdot 10^{-3}$  m/sec

#### The Extent of the Oxidational Zone and variations in space of the chemical parameters

The oxidational zone was considered to be  $R_o = 5$  m at the preliminary planning, the necessary amount of water to the enriching was  $471,2 \text{ m}^3/6$  hours, the amount of the actually dewatered water was  $430–470 \text{ m}^3/6$  hours so they correspond very well.

The results of the measurements of the  $O_2$  in solution:

producing well–8 (in recharged water):	8,6 mg/l
observation well–22. (3 m from well–8.):	3,4 mg/l
observation well–23. (6 m from well–8.):	1,2 mg/l
observation well–24. (bank filtration groundwater):	0,25 mg/l

By means of extrapolation we estimated that the  $O_2$  in solution dropped to a value of 0,25 mg/l in the vicinity of well–8. which is approximately 9,0–9,5 m (Fig. 6.).

The spatial variations of the chemical parameters show partly the theoretically probable tendencies, but partly the results have a random deviation (the values are the average of the five examinations made between 13 November 1985 – 4. September 1986).



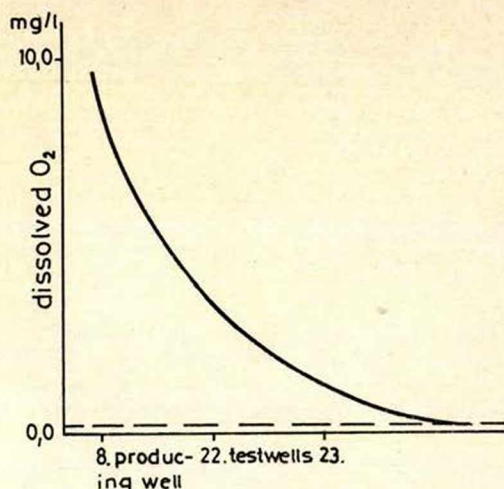


Fig.6. Change of dissolved oxygen as a function of distance from 8. producing well

observation well	alkalinity	chloride	Ca	Mg	Fe	Mn
12.	4,4	38,0	42,0	9,12	0,05	0
15.	3,8	36,4	34,07	7,9	0,02	0
19.	3,6	31,5	36,07	7,6	0,01	0
21.	4,0	24,2	31,00	7,3	0,01	0
22.	3,9	37,1	34,07	8,5	0,01	0
23.	3,5	25,0	38,08	9,1	0,01	0
24.	3,2	28,6	40,08	9,8	0,01	0

#### Maintainability of the oxidizing zone

The program of the Subterra method did not make possible the direct examination of the time of maintainability of the oxidizing zone, therefore we had to apply a complementary method.

We made the examinations at shutdowns, caused by technical problems, by means of pumping (432 m<sup>3</sup>/24 hours) in the observation wells which were at 3 metres from each other. As a simplification we agreed that the common depressed zone of the observation wells 21 and 22 is approximately equal to the zone of water-level depression by producing well 8, and the amount of water, produced in a day, is approximately equal to the fivefold amount of the recharged water for one period, in one single well.

Making the chemical analysis continuously it could be concluded that the value of iron is 0,05 mg/l after approximately 60 hours and 0,5 mg/l after some 96 hours which means that the ratio of the feed water and the produced water was 1:12 in the former case and 1:20 in the latter.

### Investigation of the extension of the area of water-table lowering in line with water production

The extension of the depressed area could be examined right angles to the Danube and to the producing well-line in two profiles, both of which gave different results.

In profiles 21-8-22-23 of the Danube (see Fig. 4) the cone of depression is characteristic of rocks with bad transmissivity;  $R$  is small,  $S_0$  is big. In profiles 12-22-15-19 the depressional cone is typical of the terrace with good transmissivity (Fig. 7). The difference is caused by the inhomogeneity of the aquifer if only it is not due to water mechanical causes.

Analysing five time profiles of water level changes and 15 profiles showing the former changes in space through the producing wells we arrived at a conclusion that the area of depression of the producing wells 2-4-6-8 and 18 are similar to each other; the area of depression is approximately 3-6 m of radius. Producing wells 10 and 30 (except for well 18) have different values, practically the depressional area extends as far as the Danube.

### INVESTIGATION OF THE IRON-MANGANESE CONTENT OF THE WATER ARRIVING FROM THE DANUBE AND FROM THE BACKGROUND

The chemical parameters of the water arriving from the background are well known. However, due to the lack of a tendency in the spatial and temporal variations in the standard deviation we can only calculate with end values and average values.

	1985				1986	
	12. June	5. Sept.	13. Nov.	30. April	14. Aug.	29. Oct.
Iron (mg/l)						
observational						
well - 2.	0,18	1,14	0,12	0,17	0,18	0,13
- 6.	0,29	0,16	0,12	0,21	0,23	0,17
- 9.	0,40	0,32	0,29	0,33	0,25	0,27
- 10.	0,12	0,21	0,17	0,13	0,22	0,20
- 11.	0,31	0,28	0,34	0,19	0,24	0,22



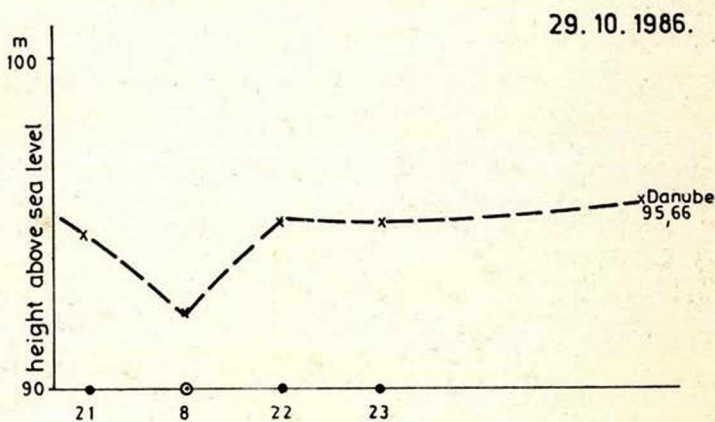
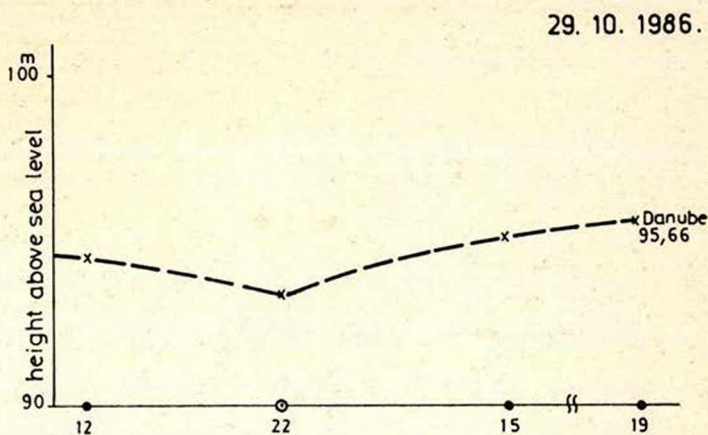


Fig. 7. Characteristic profiles at 22. and 8. producing wells

- 22., 8. producing wells
- 12., 15., 19., 21., 22., 23. testwells

## Manganese (mg/l)

## observational

well - 2.	0,11	0,18	0,21	0,17	0,19	0,14
- 6.	0,18	0,07	0,11	0,09	0,13	0,13
- 9.	0,12	0,11	0,12	0,14	0,11	0,12
- 10.	0,16	0,14	0,19	0,08	0,11	0,09
- 11.	0,11	0,13	0,13	0,18	0,08	0,10

End values: 0,12–0,40 mg/l iron  
0,07–0,21 mg/l manganese

Average: 0,22 mg/l iron  
0,13 mg/l manganese

The iron-manganese content of the water arriving from the Danube could be measured permanently in observation wells 19 and 24. In the vicinity of the producing wells the observation wells fall within the zone of the iron-manganese elimination, thus showing a smaller value.

	1985				1986	
	12. June	5. Sept.	13. Nov.	30. April	14. Aug.	29. Oct.
Iron (mg/l)						
Observation						
well - 19.	0,31	0,38	0,35	0,44	0,41	0,40
- 24.	0,28	0,48	0,43	0,41	0,44	0,37
Manganese (mg/l)						
Observation						
well - 19.	0,22	0,20	0,24	0,20	0,28	0,23
- 24.	0,24	0,29	0,25	0,24	0,26	0,22

End values: 0,28–0,48 mg/l iron  
0,20–0,29 mg/l manganese

Average: 0,39 mg/l iron  
0,24 mg/l manganese

Hence, a somewhat bigger amount of iron and manganese comes to the producing wells from the Danube than from the background. Though the difference is not big it is despite important because 80% of the water output comes from the Danube.



## INVESTIGATION OF THE EFFICIENCY OF THE IN SITU IRON-MANGANESE ELIMINATION

Under operational conditions the oxygenator gives minimum 8 mg/l  $O_2$  in solution to the recharge water, equivalent to 0,001 normality, which means that it can oxidize approximately 56 mg of iron or 274 mg of manganese in the same amount of water (1 l).

Of course, the  $O_2$  in solution satisfies also the chemical oxygen demand, oxidizes organic compounds and also other elements of changing valency but in the method under discussion its main function is the oxidation of iron and manganese.

The 8 mg/l  $O_2$  solution dessicates with 1400 m<sup>3</sup> enriching water a day. The total production of water is 3200–4600 m<sup>3</sup>/day. Subtracting the amount of the recharge water from that the net water output is 1800–3200 m<sup>3</sup>/day.

In respect of our objective it makes no difference whether we compare the amount of the recharge water to the gross or net amount of water, oversizing could easily be observed.

Disregarding the difference, due to the redox potentials which determines the order of succession of the oxidational process in this case (iron would be the first, manganese the second and later, at indefinite intervals the other effective agents of COD), the call for oxygen for 0,5 mg/l iron and 0,3 mg/l manganese is 0,115 mg/l  $O_2$ .

Multiplying that by the rate of dilution the call for  $O_2$  in solution for the oxidation of iron and manganese is maximum 0,378 mg/l at the present Subterra program and water amount, which means that the oversizing is more than twentyfold. We emphasize that the COD calls for  $O_2$  in solution which diminishes this ratio but there are obviously adsorbational catalysis and bacterial functions going on beside the direct oxidation, increasing this ratio. However the values of the latter one cannot be determined numerically.

### Summary

The in situ iron-manganese elimination process under discussion was accomplished in a technical sense; the iron and manganese content of the produced water decreased to an immeasurable value. Certain parts and parameters of the process were defined and it became clear that the applied Subterra time program is very far from being economical. By the increasing of the ratio of the produced/enriches water with an experimental value the economic index can presumably be multiplied as well.

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